



# Water dimer absorption of visible light

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## Abstract

Laboratory measurements of water vapor absorption using cavity ring-down spectroscopy revealed a broad absorption at 405 nm with a quadratic dependence on water monomer concentration, a similar absorption with a linear component at 532 nm, and only linear absorption at 570 nm in the vicinity of water monomer peaks. D<sub>2</sub>O absorption is weaker and linear at 405 nm. Van't Hoff plots constructed at 405.26 nm suggest that for dimerization,  $K_{\text{eq}}=0.056\pm0.02\text{ atm}^{-1}$ ,  $\Delta H_{301\text{ K}}^{\circ}=-16.6\pm2\text{ kJ mol}^{-1}$  and  $\Delta S_{301\text{ K}}^{\circ}=-80\pm10\text{ J mol}^{-1}\text{ K}^{-1}$ . This transition peaks at 409.5 nm, could be attributed to the 8th overtone of water dimer and the 532 nm absorption to the 6th overtone. It is possible that some lower overtones previously searched for are less enhanced. These absorptions could increase water vapor feed back calculations leading to higher global temperature projections with currently projected greenhouse gas levels or greater cooling from greenhouse gas reductions.

## 1 Introduction

The balance of energy between incoming radiation to the earth and blackbody radiation emitted by the earth and absorbed by the atmosphere critically affects global temperatures and is calculated by models of radiative forcing. Water vapor feedback has a positive effect on global temperatures (Held and Soden, 2000), but the magnitude of this effect is 2 to 3 times stronger than models predict (Fomin and Udalova, 2003; Philipona, 2005; Durr et al., 2005). One component of water vapor feedback is direct absorption. An, as yet unidentified, absorption in the short wavelength region has been predicted by Arking from modeling and long path-length measurements in the atmosphere. The resulting estimation of  $15\text{--}30\text{ W m}^{-2}$  could cause a difference of  $4^{\circ}\text{C}$  in the calculated average surface temperature of the earth (Carlson, 1979; Arking, 1996, 1999). Observations of this anomalous absorption found that the discrepancy was measurable in tropical regions and near clouds (Hill and Jones, 2000), but were

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complicated by the presence of scattering by particulates. Potential sources of the additional absorption include absorptions due to water dimer and water far wing continuum absorption. Water dimer has been calculated to absorb  $3\text{--}6\text{ W m}^{-1}$  of solar radiation from calculations that used an outdated model for Helium clusters (Tso et al., 1998), and were then recalculated to be less (Vaida, 2001; Daniel et al. 2001). A third paper suggested that vibrational levels above the dissociation limit make the absorptions even stronger (Schenter, 2002; Kathmann et al., 2002). The results of this study suggest the absorption might actually be higher, but it is not clear whether levels above the dissociation limit are enough to explain the magnitude of the measurements by our laboratory (Hargrove, 2006; Wang et al., 2006), and an additional theoretical mechanism might need to be invoked to explain these results. This paper further explores this water absorption and establishes some evidence that it is due to water dimer.

Water vapor continuum absorption has been measured previously, but only in the microwave, infrared and near infrared regions of the spectrum (English, 1994; Guillou et al., 1994; Hewison 2006). In the near infrared, Sierk et al. reported water dimer absorption between 880 and 1000 nm using differential optical absorption spectroscopy (DOAS) (Sierk, 2004; Solomon et al., 2004), since then Cormier et al. have done a meticulous study of water vapor continuum absorption at 944 nm determining additionally the effect of water nitrogen complexes and water oxygen complexes using cavity ring-down spectroscopy (CRDS) (Cormier, 2005; Hodges et al., 2005). Notably, in 2003 a water vapor band was mistakenly attributed to water dimer (Pfeilsticker, 2004; Lotter et al., 2003), but was shown to be too narrow to be water dimer (Pfeilsticker, 2004). It may be that attempts to observe lower overtones of water dimer have been unsuccessful due to a cancellation effect of the water dipoles that was noticed in intramolecular hydrogen bonded species (Howard and Kjaergaard, 2006). At 750 nm the water vapor continuum was determined to be not detectable by CRDS (Kassi, 2005; Macko et al., 2005) Carleer et al. (2003) measured a broad feature in the visible spectrum of water and attributed it to possible scattering by  $1\text{ }\mu\text{m}$  water droplets and noted correctly that this is unlikely because their measurements were taken at water concentration levels

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well below saturation. In this study, the possibility of scattering by droplets and mirror absorption were both checked and eliminated as a source of the signal. This study attempted to measure the enhancement of water dimer absorption at 397–532 nm and the lack of water dimer absorption at 570 nm.

## 2 Materials and methods

For these experiments water vapor was generated by bubbling zero grade air through Millipore purified water with a resistivity greater than 15 mega ohms or EMD brand OmniSolv water in a micro-impinger held at constant temperature. D<sub>2</sub>O was obtained from Acros with 99.8 atom% D. The water was degassed by bubbling zero grade air through the impinger at temperatures above 70°C for 10 min. Impurities were noted in the Millipore water from liquid phase spectra that were concentrated by the degassing procedure suggesting that they remained in the water. The impurities were absent in the OmniSolv water, and the cross section in the gas phase was not affected by the water source. When the water level was low in the bubbler, it was possible to obtain low readings due to lower levels of saturation, and when bubbles were not avoided the readings became high due to droplets of water depositing downstream of the low temperature region of the bubbler. For this reason a dew point hygrometer was added inline downstream of the CRDS sample cell to measure the resulting water vapor concentration. A third complication was that initial readings were sometimes high particularly after measurements of ambient NO<sub>2</sub> and calibration gas possibly due to out-gassing of NO<sub>2</sub> from the system that leveled out consistently within three measurements to the same levels as more water vapor was put through the system. A flow rate of 0.25 L min<sup>-1</sup> was found to be optimal to avoid bubbles. Approximately 15 feet of Teflon tubing led from the bubbler to a 0.45 μm filter at the inlet of the sample cell allowing for some time for the temperature to return to the 21°C ambient level of the room. To reach elevated temperatures, an empty glass trap was added after the filter and heated in a water bath to the required temperatures along with heating tape to heat the sample cell.

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In recent years, CRDS has been applied in many reported studies and the details of operation have been reported previously (Wang and Zhang, 2000; Hargrove, 2006; Wang et al., 2006). The thousands of reflections that occur in the optical cavity enhance CRDS sensitivity. The rate of decay of the light is measured rather than the magnitude of attenuation to minimize the effect of light intensity variations. The dry air filled cavity rate of decay is subtracted from the sample rate of decay and divided by the speed of light to obtain the absorption coefficient. Near-UV laser radiation in the region of 405 nm (1–2 mJ/pulse, line width 0.2–0.3 cm<sup>-1</sup>) was generated from frequency doubling the ~810 nm output of an Nd:YAG 532 nm-pumped dye laser (LDS 798 and LDS 821 dyes). The cavity mirrors have reflectivity better than 99.995% at 405 nm (Research Electro-Optics, diameter = 20 mm, and radius of curvature (ROC) = 1 m). The ring-down signal was collected on a 14-bit 200 MS/s oscilloscope card (Gage) and each ring-down event was curve fitted before averaging. To achieve this, a fast algorithm developed by Halmer and von Basum (2004) written in C++ was used in combination with data collection software written in house starting from the Gage software development kit using National Instruments Labview v.7.1. Experiments using the buffer chambers involved providing two additional inlets and outlets for the chamber and matching the flow rates into and out of the three regions of the sample chamber to minimize mixing between the regions. For temperature controlled studies the entire chamber was wrapped with heating tape. The center glass tube and steel end chambers were controlled separately with two Variacs and kept within a few tenths of a degree from each other. Soft large O-ring seals at the mirrors limited the upper temperature obtainable to 35°C, but since there was a significant drop in signal even at 35°C a high temperature cell was deemed unnecessary. Spectra were taken in three parts with measurements taken at the endpoints of the spectra to correct for baseline drift by subtracting values from the baseline and interpolating. Noise in the spectra was enhanced relative to other experiments because the scanning process takes considerable time. With this technique a tradeoff has to be made between better noise in a slow scan and less baseline drift in a fast scan.

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3 Results and discussion

Ambient measurements of NO<sub>2</sub> at 405 nm found that there was interference from water vapor (Hargrove, 2006; Wang et al., 2006). The scans taken from 410 nm down to 397 nm (24 400 to 25 200 cm<sup>-1</sup>) show a broad absorption without significant structure. Shorter scans showed some evidence of water monomer peaks below 400 nm but were not well resolved from the noise. Water monomer peaks have been detected previously in this region (Dupre, 2005; Gherman et al., 2005; Tolchenov, 2005; Naumenko et al., 2005), mostly below 400 nm. Multiple scans were conducted and yielded a minimum at 400 nm (25 000 cm<sup>-1</sup>) and a peak at 409.5 nm (24 420 cm<sup>-1</sup>) that contained no evidence of NO<sub>2</sub> features from any contamination. The limit of detection in this region was 2.6×10<sup>-9</sup> cm<sup>-1</sup> for 10 s of averaging. Further averaging of 9 points each was used to obtain the Beer-Lambert plots, corrected baseline, and temperature dependence.

Three aspects of the water absorption were examined at 405 nm: the absorption spectrum to study the breadth of the absorption, the water monomer concentration dependence, and the temperature dependence to test the possibility of water dimer as a source of the signal. At 532 nm the concentration dependence was established but temperature dependence was not attempted because the temperature dependence would require measurements at multiple concentrations and curve fitting to remove the linear component, and would require better sensitivity. Wavelength dependence could not be studied at 532 nm because the measurements were not taken with a tunable laser. This would be an interesting topic for future study. The absorptions at 405 and 532 nm are not likely due to water monomer, as water monomer has sharp absorptions to the red and blue of 405 nm and 532 nm that do not overlap. The absorption at 405 nm could be attributed to either water dimer absorption or water vapor far wing continuum absorption due to water collisions with water molecules. Far wing continuum theories likely would predict a much weaker absorbance, with stronger absorptions to the red, though modeling of this effect is ongoing. Far wing continuum may cause the linear component at 532 nm but better sensitivity is needed before temperature dependent

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studies will be useful. The continuum at 570 nm is linear with respect to monomer (Fig. 2), has no temperature dependence, and is just between two water monomer peaks (Fig. 3). The source of this absorption is not clear, but could be due to collisions. So three regions were present where absorption was measurable the next step was to measure the dependence on water monomer concentration.

The dependence of the absorption on water monomer concentration was the first indication that water dimer might be involved. At 405 nm there is a simple quadratic dependence suggesting that only water dimer contributes to the signal. At 532 nm there seems to be a mix of water dimer absorption and water monomer absorption resulting in a curve that does not follow a simple quadratic dependence i.e. there is a linear component. At 570 nm the response is apparently linear despite some noise during data collection (Fig. 2). The limit of detection in these measurements was  $2.6 \times 10^{-9} \text{ cm}^{-1}$  and was signal averaged to obtain background noise less than  $1 \times 10^{-9} \text{ cm}^{-1}$ . The extra noise in the 570 nm linearity data was due to uneven baseline drift during measurements that day. Baseline drift was often a problem and motivated the development of a rigid sample cell with low thermal expansion for future studies. Despite these problems it was clear that no evidence of water dimer absorption was present at 570 nm. The  $0.3 \text{ cm}^{-1}$  line widths of the water monomer peaks at 570 nm were used to verify that water monomer peaks at 400 nm would be difficult to observe relative to the noise.

Though it is agreed that water does dimerize in the gas phase, there has been controversy over whether water dimer contributes to continuum absorption, because bound states might not be thought to produce strong or broad spectra (R. Tipping, personal communication). However, water dimer vibrational transitions would be expected to show a greater density of states and the resulting spectra would be broadened by predissociation. The broad absorption at 409 nm showed a negative temperature dependence as would be expected for dimer absorption (Fig. 4). At 405.26 nm, van't Hoff plots were constructed over a temperature interval of 21°C to 35°C and the equilibrium constant of dimerization and dimer cross section were reiteratively calculated resulting in equilibrium constant of  $K_{\text{eq}} = 0.056 \pm 0.02 \text{ atm}^{-1}$ , water dimer cross section of

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$3.8 \times 10^{-22} \text{ cm}^2 \text{ molecule}^{-1}$ , enthalpy change of  $-16.6 \pm 2 \text{ kJ mol}^{-1}$ , and entropy change of  $-80 \pm 10 \text{ J mol}^{-1} \text{ K}^{-1}$ .

The possibility of other water containing clusters was considered. A cluster with another species like  $\text{NO}_2$  would have to contain 2 water molecules to produce the quadratic response and thermodynamics observed. It is likely that the bonding would be similar to water dimer but with one component at trace levels so that the concentration would be exceedingly small. It was calculated that the  $\text{NO}_2\text{H}_2\text{O}$  trimer would be  $\sim 1800$  times less abundant than the individual pair and could be the only significant chromophore to get simple quadratic absorption. Thus, for this data to come from clusters of water with other species like  $\text{NO}_2$  would be exceedingly unlikely.

Two tests to evaluate the possibility of surface absorption on the ring-down cavity mirrors found no evidence of surface-absorbed water light absorption. The first test measured the water response in the presence of added buffer chambers at each end of the sample cell. The only loss of signal was equivalent to the loss of path-length by the addition of the buffer chambers. Also, heating the mirrors to  $40^\circ\text{C}$  had no effect on the signal. The cross section at  $405 \text{ nm}$  would correspond to  $1 \text{ mm}$  of liquid water on each mirror (Sogandares and Fry, 1997), so any mirror sorption should not be detectable unless there is an unusual thin film effect on the mirror reflectivity, which was ruled out by these tests.

As an additional check of the mechanism, measurements were taken with  $\text{D}_2\text{O}$  in place of  $\text{H}_2\text{O}$ .  $\text{D}_2\text{O}$  would be expected to absorb at longer wavelengths so that the measurements should be off-peak. The absorption due to  $\text{D}_2\text{O}$  at  $405 \text{ nm}$  was actually measurable. It was linear with respect to concentration, and increased smoothly to the blue ( $1.0 \times 10^{-25} \text{ cm}^2 \text{ molecule}^{-1}$  at  $405 \text{ nm}$  and  $1.6 \times 10^{-25} \text{ cm}^2 \text{ molecule}^{-1}$  at  $397 \text{ nm}$ ). It is surprising that the cross section is as high as it is but it is still lower than for  $\text{H}_2\text{O}$ .  $\text{D}_2\text{O}$  has a lower vapor pressure than  $\text{H}_2\text{O}$  so any Mie scattering by water droplets or surface effect should be stronger with  $\text{D}_2\text{O}$ . The linear water monomer dependence suggests that there was no  $\text{D}_2\text{O}$  dimer measurable at  $405 \text{ nm}$  as expected. This low  $\text{D}_2\text{O}$  response helped rule out the possibility of droplet and surface absorption artifacts.

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5 The thermodynamics of water dimer formation in the atmosphere has been the subject of several calculations (Schenter et al., 2002, 2003; Goldman, 2004, 2005; Lefor-  
 10 estier et al., 2004, 2005). The most recent (Scribano, 2006; Goldman et al., 2006) suggest that in this temperature range  $\Delta H = -19.2 \text{ kJ mole}^{-1}$  and  $\Delta S = 90 \text{ J mol}^{-1} \text{ K}^{-1}$  producing an equilibrium constant in agreement with ours ( $0.051 \text{ atm}^{-1}$  vs.  $0.056 \text{ atm}^{-1}$ ).  
 It has been difficult to confirm these calculations previously due to the lack of spectroscopic data on the dimer. The dissociation energy agrees with previous measurements by thermal conductivity (Curtiss, 1979; Frurip et al., 1979), an extrapolation of the analysis of the 3rd order term of the virial equation for steam to room temperature (Slanina  
 10 et al., 2006), and the recent spectroscopic measurements (Ptashnik et al., 2004). The cross section and equilibrium constant calculated in this paper are both perhaps surprisingly high. The equilibrium constant is in agreement with theory and the cross section may have been enhanced by the greater density of states above the dissociation limit (Schenter et al., 2002). From the nature of the measurements it is implied that  
 15 if either is actually smaller then the other is correspondingly larger, notwithstanding any measurement errors.

The simple quadratic absorption at 405 nm and the enthalpy and entropy calculated from the van't Hoff analysis are consistent with water dimer as the source but do not exclude the possibility of far wing continuum absorption. The greater density of states  
 20 present in the dimer configuration could enhance the vibrational overtone bands of water dimer. Periodic shifting of charge density within the dimer may also enhance absorption. There is a shift in the water dimer wavefunctions in the overtones due to an unusual anharmonicity effect starting near the  $v=6$  level that may cause lobes of the  
 8th overtone to overlap significantly with the ground state wavefunction (Huang et al., 2006; Schofield et al., 2007). This could partly explain the relatively large magnitude of the  $\sim \Delta V=8$  absorption at 405 nm in comparison to the  $\sim \Delta V=6$  absorption at 532 nm. The  $v=7$  overtone should be measurable at about 440 nm and comparable absorption  
 25 has been observed with a diode based cavity attenuated phase shift (CAPS)  $\text{NO}_2$  detector operating from 430–450 nm (A. Freedman, personal communication).

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Remarkably, the dimer cross section at 405 nm is  $10^5$  times stronger than that of liquid water (Sogandares and Fry, 1997). This appears to be due to a shift in the frequency and enhancement in the magnitude of the overtone transitions involved. It is unlikely that this feature is due to Rayleigh scattering of water vapor, because the Rayleigh scattering cross-section for water vapor is less than that of nitrogen or oxygen (Tomasi et al., 2005). Mie scattering by droplets is also unlikely. Droplets would have to pass through or be generated by the  $0.45\text{ }\mu\text{m}$  filter used immediately upstream in this study. A filter of this type is commonly attributed to remove particles an order of magnitude smaller than the pore size, and if it were possible for droplets to be generated from the surface of the filter, the droplets would likely be formed for some time after switching to the baseline. Tests without the filter also showed the same cross section. Ambient tests with  $\text{NO}_2$  removed by a denuder coated with sodium hydroxide and guaiacol showed absorption consistent with water dimer at the local humidity level.

One consequence of this absorption is that ambient measurements of trace gasses by optical spectroscopy may have to account for water vapor interference. More significant, however, is the consequence for radiative forcing calculations. A significant portion of the  $15\text{--}30\text{ W m}^{-2}$  discrepancy between the calculated and actual amount of radiation absorbed by the atmosphere could be due to water dimer absorption. The large magnitude of the signal at 405 nm, and the signal at 532 nm  $\sim 5$  times that of Tso et al. (1998) ( $2.7 \times 10^{-22}\text{ cm}^2$  cf.  $6 \times 10^{-23}\text{ cm}^2$ ), even with the greater density of states above the dissociation limit (Schenter et al., 2002) is hard to justify. The additional absorption at 405 nm is beyond  $20\,000\text{ cm}^{-1}$  as well, was not considered in their estimate, and will contribute a similar amount of additional absorption. Calculations of the water dimer cross section from a 1-dimensional potential (Schofield et al., 2007) and extended to  $\Delta v=8$  have resulted in very small oscillator strengths ( $10^{-13}$ ), but more recent calculations based on the full potential energy surface (Huang et al., 2006) have been closer ( $10^{-10}$ ). However, these calculations still do not agree due to the broad nature of the absorption that could add another three orders of magnitude to the measured oscillator strength. These cross sections may seem unreasonable, but it has

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been shown that good cross sections for NO<sub>2</sub> can be obtained with this instrumentation in the same region of the spectrum. It is anticipated that other groups will not have difficulty reproducing these measurements.

5 The consequence of these absorptions in the atmosphere will be an increase in calculated positive water vapor feedback, though another additional effect may be cooler surface temperatures and warmer air temperatures. If global warming continues as is anticipated, the increased air temperatures will lead to greater levels of water vapor in the atmosphere. With greater levels of water vapor the increase in water dimer will be nearly quadratic, and increase the direct absorption of sunlight to a greater extent  
10 than would be predicted by empirical models based on water monomer absorption and line broadening. This would be offset partially by the shift in equilibrium at higher temperatures to favor water monomer, but the net result would likely be to enhance the warming effect. Conversely, if greenhouse gasses subside, the result would be to enhance the cooling effect. The calculations required to model this system have not yet  
15 been undertaken and will require accurate cross sections at all relevant wavelengths and an accurate model of the thermodynamics. It is hoped that in the near future these factors will be determined with higher precision and applied to predict future global temperatures with greater accuracy. It has been recently reported that climate change is happening faster than current models predict (Rahmstorf et al., 2007) so it is possible  
20 the effect of this water absorption needs to be taken into account.

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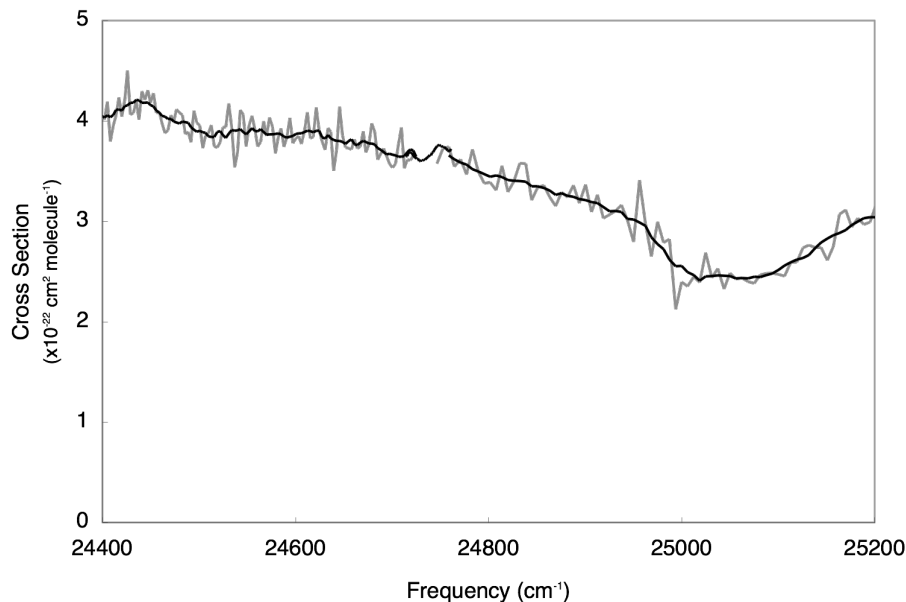
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**Fig. 1.** The spectrum of water dimer near 405 nm, showing the junction of a pair of broad absorption features with a minimum near  $25\,000\text{ cm}^{-1}$ , and unexpectedly high cross sections. The solid line shows 9 point smoothing of the raw data in grey.

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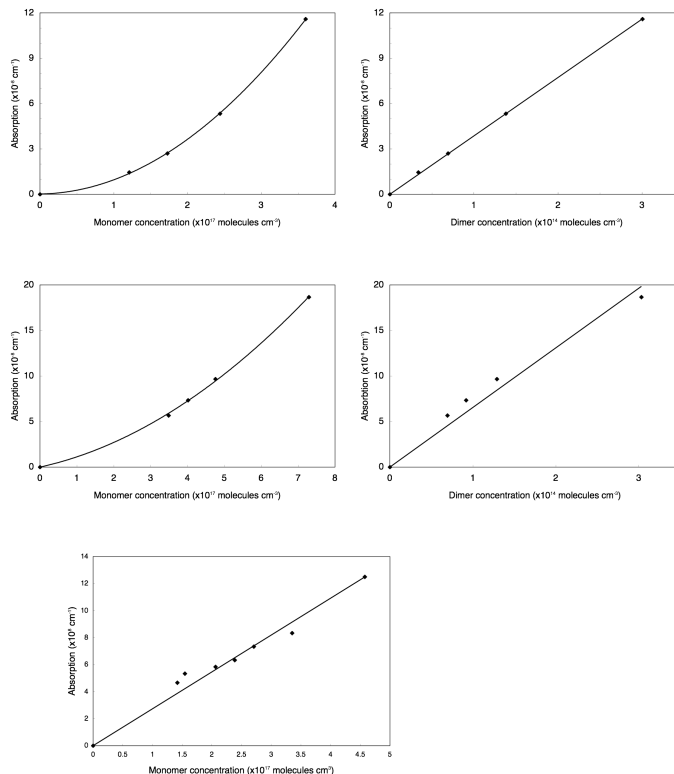
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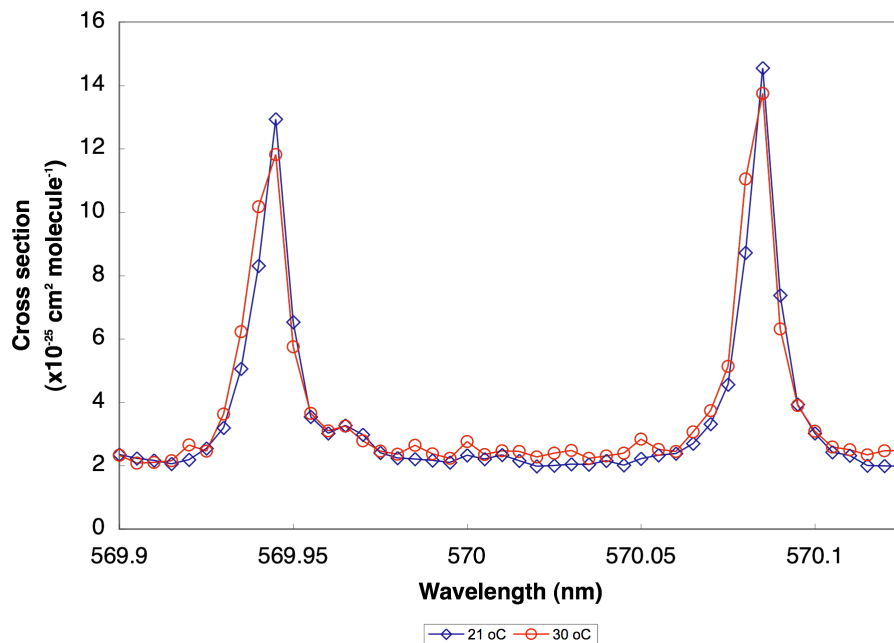
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**Fig. 2.** Beer-Lambert law plots assuming absorption due to **(a)** water monomer and **(b)** water dimer at 405 nm **(c and d)** 532 nm and **(e)** monomer at 570 nm. There is a simple quadratic dependence at 405 nm. The water dimer graph calculated using the equilibrium constant we obtained follows the Beer-Lambert law with a dimer cross section of  $3.8 \times 10^{-22} \text{ cm}^2 \text{ molecule}^{-1}$ . At 532 nm, a linear term is present in the monomer plot yielding a monomer cross section of  $1.5 \times 10^{-25} \text{ cm}^2 \text{ molecule}^{-1}$  and dimer cross section of  $2.7 \times 10^{-22} \text{ cm}^2 \text{ molecule}^{-1}$ . At 570 nm only a linear  $1.0 \times 10^{-25} \text{ cm}^2 \text{ molecule}^{-1}$  continuum is present.

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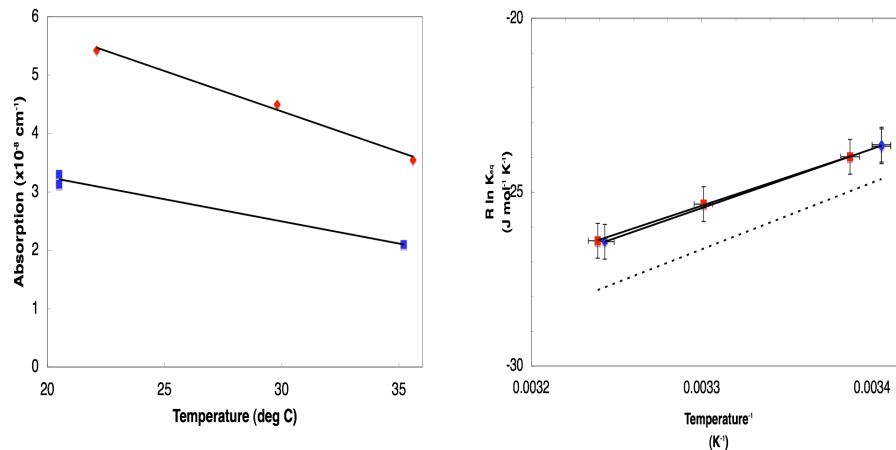


**Fig. 3.** Absorption at 570 nm showing a broad continuum shift in the baseline with no temperature dependence or quadratic response in contrast to that at 410 nm. The peaks present show a predictable broadening and shift to the blue as would be expected at higher temperatures.

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**Fig. 4.** Van't Hoff plot: Two experiments were performed with constant water vapor concentrations at a dew-point of 10 $^{\circ}\text{C}$  (blue) and then 15 $^{\circ}\text{C}$  (red). The enthalpy matches previous experiments and the equilibrium constant is close to the theoretical value of Scribano et al. but lower than the enthalpy and entropy (dotted line).

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